

Effect of Gas Composition on Compression Sensitivity of Liquids(1)

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The ignition of liquid explosives and propellants by the rapid compression of gas bubbles has been studied extensively both because of scientific interest and because of immediate needs for devising safe operating procedures and for estimating the sensitivity of new materials (1,2,3,4,5)(3). Two explosions of tank cars of nitromethane that might have been initiated by this mechanism have occurred in recent years, as have a number of smaller accidental explosions in the testing of experimental propellants.

Nature of the Ignition Process

In the simplified model of the ignition of a liquid explosive by adiabatic compression of an entrapped gas bubble, the temperature is considered to increase during compression according to the relation:

$$\frac{T}{T_0} = \left(\frac{P}{P_0}\right)^{\frac{\gamma-1}{\gamma}} \quad [1]$$

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When a sufficiently high temperature is reached in the gas, it is postulated that ignition of explosive vapor in the bubble occurs, further raising the temperature at an exponentially increasing rate. At this stage the process becomes self-sustaining through the evaporation and reaction of fresh material surrounding the heated region.

An exact analysis of the process cannot be made because of uncertainties about the exchange of heat and mass between the liquid and gas and the configuration of the liquid-gas interface during compression.

From the assumptions of adiabaticity and a characteristic minimum ignition temperature in the compressed bubble, it follows that the energy required for ignition is related to the initial conditions in the bubble by the expression for compressive work in an adiabatic non-flow process:

$$W_i = \frac{P_1 V_1}{\gamma - 1} \left(1 - \frac{T_1}{T_0} \right) \quad [2]$$

Changes in the gas specific heat ratio, γ , should therefore affect the minimum ignition energy in inverse ratio to $(\gamma - 1)$. Also, the minimum ignition energy should be proportional to the initial bubble volume.

Experimental Procedure

The equipment and operating procedure have been described in detail previously(2,5).

The sample, consisting of a bubble in contact with liquid, is compressed by a gas driven piston. The sample chamber is one-half inch in diameter, with a total volume of about 1.5 ml. It is sealed with either a steel or aluminum burst disc that can contain static pressures above 20,000 psi.

All combinations of liquid and gas were tested at least three bubble volumes, 0.2, 0.4, and 0.8 ml. A reversal procedure was used to estimate minimum ignition energy at each bubble volume, first determining an approximate range, in terms of driving pressure, and then proceeding to vary driving pressure in small even increments up or down, depending on whether the preceding result was positive or negative. Usually each reversal series included at least six tests.

The energy of the piston is calculated by a derived expression in terms of the physical properties of the equipment, corrected by an empirical factor obtained from direct measurements of piston velocity. The accuracy of the energy estimate is about $\pm 15\%$.

To put gases other than air in the chamber, the area around the open sample chamber was loosely covered with a clear plastic cone with the point cut off. Purge gas entered through the side of the cone. Liquid sample was put in through the open end. The burst disc was then dropped in place, the cone removed, and the disc retainer bolted down.

To load a sample consisting of liquid and its own vapor, the piston was retracted far enough so that the chamber volume was equal to the desired amount of liquid. The chamber was then sealed with a burst disc and the piston retracted fully, leaving a vapor space of known volume above the liquid.

Test Results

Minimum ignition energies were determined for nitromethane with bubbles of air, oxygen, nitrogen, argon and carbon dioxide. Samples could not be made to ignite in the presence of nitromethane vapor alone. Results are shown in Table 1 in terms of minimum ignition energy per unit bubble volume, in kg-cm/ml. This was found to be constant for each liquid-gas volume combination, within limits of experimental error, with two exceptions out of a total of seventeen test groups.

Assuming that the minimum ignition energy for argon truly corresponds to a minimum temperature for ignition in the compressed bubble, minimum ignition energies were calculated for the other bubble gases by Eq.(2), and are also shown in Table 1.

The agreement between the observed and calculated values for the inert gases is nearly within the limits of experimental accuracy.

The inability to ignite the sample with only nitromethane vapor in the bubble can be explained on the basis of rapid condensation of the vapor in the liquid during compression.

Oxygen has a strong sensitizing effect, as shown by results with air and pure oxygen. The effect apparently reaches a maximum at some concentration below that of atmospheric air. This result, together with the observed effect of specific heat ratio with the inert gases, strongly indicates that the ignition of nitromethane, and presumably other C-H-O-N compounds, can start in the vapor phase by reaction with gaseous oxygen.

A related effect of oxygen concentration on the sensitivity of solid double-base propellants to ignition by detonating gas mixtures was found by Cook(3), so the possibility of reaction of the condensed phase surface with the gaseous oxidizer has been amply demonstrated.

The ignition temperatures calculated on the basis of an adiabatic process appear somewhat high for the inert gases, but reasonable for air and oxygen.

To get comparable data on a material qualitatively different in physical and chemical properties from nitromethane, tests were made on a nitric acid composite very similar to a Sprengel-type explosive. The vapor above the liquid is non-explosive at ordinary temperatures, since the vapor pressure of the fuel component is negligible.

Gases used in the tests were air, nitrogen, argon, carbon dioxide, and nitric acid vapor. Results are shown in Table 2.

The most significant result is that ignition could be obtained consistently, and that the energy required was not particularly large.

No differences in energy input between argon and nitrogen or air were detected. Carbon dioxide affected sensitivity measurably, although to a lesser extent than predicted. Calculated adiabatic ignition temperatures do not appear unreasonably high compared to those for nitromethane, but they lack quantitative significance because of the necessity for heat transfer in the ignition process. The only available explanations for ignition under these conditions are that the liquid got hot enough to react or that fuel was transferred to the vapor phase by non-equilibrium evaporation.

Evans and Yuill(6) have observed similar ordering of calculated temperatures in the ignition of nitroglycerine and PETN by compression of oxygen, air, nitrogen and argon, with the difference that the sensitivity of PETN is increased markedly in the presence of pure oxygen. The same authors report also the ignition of a number of solid explosives that have negligible vapor pressure.

If the requirement for ignition is that a surface layer of liquid reach some minimum temperature, this would largely account for the observation that the energy input required is only slightly affected by the specific heat ratio of the gas.

The total energy input in most of the tests described here is enough to evaporate a few milligrams of explosive; the mass of gas in the bubble is about one milligram. Some evaporation of the sample is thus possible during compression, and this would further tend to diminish the effect of gas specific heat on minimum ignition energy.

Conclusions

Bubble gas composition has a pronounced effect on compression sensitivity, even of liquids having non-explosive vapor under ordinary conditions.

Oxygen, in atmospheric concentration and greater, has a strong sensitizing effect on nitromethane and therefore probably on other C-H-O-N propellants and explosives. This observation, and the observation that minimum ignition energy can be correlated with gas specific heat ratio, strongly indicate that ignition of nitromethane and other volatile materials starts in the vapor phase, by reaction with oxygen if it is present.

Since materials that under ordinary conditions have a non-explosive vapor can be ignited, heat transfer, possibly accompanied by mass transfer, can take place across the gas-liquid interface at a significant rate during compression.

At least three factors can contribute to ignition. These are reaction in the gas phase, reaction at the surface with the gas phase, and reaction at the surface of the condensed phase caused by heat transfer from the compressed gas phase. There is also the possibility of mass transfer from the condensed phase to the gas phase, followed by reaction in the gas phase, although this is not a prerequisite for ignition. The nature of both the gas and the condensed phase determine which effect or combination of effects will predominate in any given ignition process.

The hazard of accidental ignition of liquid explosives initiated by the mechanism of rapid compression can be reduced by control of the composition of gas in contact with the liquid. Desensitizers should have high vapor pressure and specific heat, should be miscible to some extent with the liquid, and should be chemically inert toward the liquid.

Nomenclature

T = temperature

P = pressure

γ = specific heat ratio

W = energy input to sample

V = bubble volume

Subscripts

i = minimum required for ignition

o = initial condition

References

- (1) BOWDEN, F. P. and YOFFE, A. D.
"Initiation and Growth of Explosion in Liquids and Solids"
University Press, Cambridge (1952).
- (2) "Liquid Propellant Test Methods Recommended by the JANAF
Panel on Liquid Propellant Test Methods"
The Liquid Propellant Information Agency, Applied
Physics Laboratory, The Johns Hopkins University.
- (3) COOK, M. A.
"The Science of High Explosives"
Reinhold Publishing Corp., New York (1958).
- (4) GRIFFIN, D. N.
"The Initiation of Liquid Propellants and Explosives by
Impact"
ARS Paper No. 1706-61, presented at the ARS Propellants,
Combustion and Liquid Rockets Conference (April 26-28,
1961).
- (5) MEAD, G. A.
"Compression Sensitivity of Monopropellants"
ARS Journal, Vol. 29, No. 3, p. 192 (1959).
- (6) EVANS, J. I. and YUILL, A. M.
"Initiation of Condensed Explosives by Compression of the
Surrounding Gas"
Proceedings of the Royal Society of London, Series A,
Vol. 246, p. 176 (July 1958).

Table 1. Effects of Gas Properties on the Compression Sensitivity of Nitromethane

Bubble gas	Specific heat ratio, γ *	Measured sensitivity, kg-cm/ml	Calculated sensitivity relative to argon **, kg-cm/ml.	Ignition temperature, °K, calculated on the basis of measured sensitivity
Oxygen	1.34	10.4 ± 1.1	45	730°
Air	1.37	10.9 ± 1.1	42	900°
Nitrogen	1.37	40 ± 6	42	4000°
Argon	1.67	23 ± 3	23	4200°
Carbon dioxide	1.20	105 ± 15	77	5800°
Nitromethane	1.09	> 120	9	> 70,000°

* At 700°K, arbitrarily taken as an average value.

** On the basis that the value measured for argon represents the true minimum ignition temperature.

Table 2. Effects of Gas Properties on the Compression Sensitivity of a Composite Explosive

Bubble gas	Specific heat ratio, γ *	Measured sensitivity, kg-cm/ml	Calculated sensitivity relative to argon **, kg-cm/ml	Ignition temperature, °K, calculated on the basis of measured sensitivity
Air	1.34	21 ± 2	47	1770°
Nitrogen	1.37	26 ± 4	44	2500°
Argon	1.67	24 ± 3	24	4400°
Carbon dioxide	1.20	35 ± 5	80	1730°
Vapor	1.11	81 ± 12	10	> 39,000°

* At 700°K, arbitrarily taken as average value.

** On the basis that the value measured for argon represents the true minimum ignition temperature.